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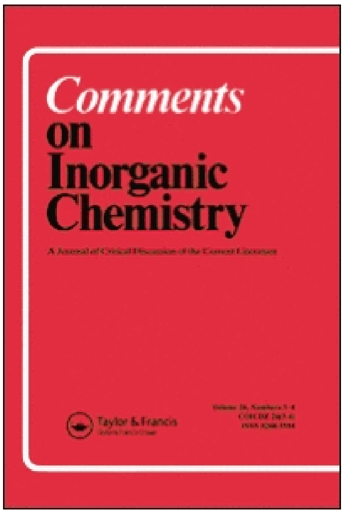

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Intercalation Chemistry: Electron/Ion Transfer Reactions

Intercalation reactions of host lattices with electronic conductivity that proceed via electron/ion transfer have received increasing attention in the last decade both for their basic research interest as well as for possible technological application. Present concepts provide the basis for a qualitative understanding of these complex systems.

INTRODUCTION

Crystalline solids are characterized by a regular spatial array of atoms which above $T = 0$ K are subject to periodic motions in their potential wells. Solid state reactions therefore require as a rule high temperatures close to the melting point, where the concentration of thermodynamic equilibrium defects becomes significant and aperiodic motions (diffusion) of lattice constituents appear. There are, however, exceptions: solid state reactions that proceed at relatively low temperatures. Among these are the so-called *intercalation reactions* which usually occur at or close to room temperature. The latter represent a unique group of solid state reactions which are of particular interest for various reasons discussed below.

If we use a most simple model we can describe the intercalation process by the (reversible) insertion of mobile guest species (atoms or

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molecules) into a solid host lattice that contains an interconnected system of empty lattice sites of appropriate size:

$$x\,\mathrm{A} + [\mathrm{Z}] \rightleftarrows \mathrm{A}_x\,[\mathrm{Z}]. \tag{1}$$

$$(\mathrm{A} = \text{ guest species, } \mathrm{Z} = \text{ host lattice})$$

This reaction is a topotactic process, as the structural integrity of the host lattice is conserved in the course of the forward and reverse reaction. A large number of host lattices has been studied with different structural dimensionality: framework structures containing empty channels for the uptake of guest species (e.g., zeolites WO_3, Mo_6S_8), layered structures that can accommodate guests in the van der Waals gap between the sheet units (e.g., layered silicates, graphite, MoO_3, transition metal dichalcogenides) and chain structures able to take up guest species between the one-dimensional matrix units (e.g., transition metal trichalcogenides, Mo_3Se_3, $RuBr_3$) (Figure 1). Similarly, a large variety of atomic or molecular guest species has been described which can be intercalated by direct insertion or exchange reactions either as neutral units (e.g., H_2O, NH_3, polar organic molecules) or as ionic species (e.g., metal cations, H^+, metal complex cations, organic protonated or quaternary ions) depending upon the type and structure of the host lattice.

Recent interest in these phases has focused largely on the following aspects: (i) phase ranges, structure and ordering states, reaction mechanisms, nature of interaction between host lattice and guest species, (ii) temperature dependent dynamics of guest species and anisotropy phenomena, (iii) changes in physical properties of the host lattice upon intercalation, (iv) application of intercalation compounds (selective sorption and ion exchange, reversible battery electrodes, heterogeneous catalysis, electrocatalysis, etc.). The large body of information that has accumulated by now is accessible in a series of recent reviews and monographs.[1-9]

Particular attention has been devoted in the last ten years to host lattices which exhibit electronic conductivity. These are able to intercalate guestions by *electron/ion transfer* reactions according to Eq. (2)[6,7]:

$$x\,\mathrm{A}^+ + x\,e^- + [\mathrm{Z}] \rightleftarrows \mathrm{A}_x^+[\mathrm{Z}]^{x-}, \tag{2}$$

which can readily be controlled and studied by electrochemical techniques. The equation given for this process obviously implies quanti-

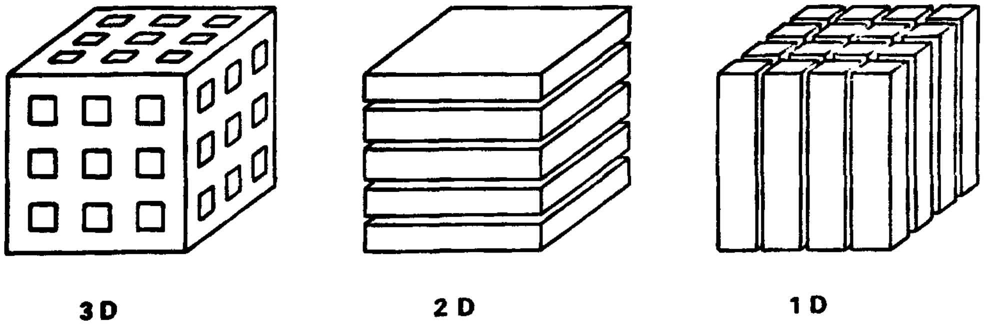


FIGURE 1 Scheme of host lattice types with different structural dimensionality.

tative transfer of the electrons to the host lattice matrix which thus becomes a macroanion with mobile negative screening charges. Although this model seems to be essentially correct for the majority of systems investigated, recent studies have yielded evidence that there are many border cases which have to be described by more refined concepts, e.g., electron storage in metal–metal bonds between guest ions. A further problem was the nature of the interaction between host lattice and guest species in those cases where spontaneous reaction of neutral molecular guests with neutral empty host lattices was observed. Recent investigations reveal, however, that this process also involves complex redox reactions.[6,10,11] These observations have led the author to the general concept that "all primary intercalation processes of host lattices which exhibit electronic conductivity (or become electronic conductors upon intercalation) are topotactic redox reactions."

Since the problem of charge transfer is directly related to the understanding of structure, physical properties, transport phenomena, chemical reactivity and reaction mechanisms of these compounds, it is the purpose of this Comment to summarize the present status of our knowledge on this subject.

INTERCALATION OF METAL GUEST IONS

The most simple model for electron/ion transfer reactions is described by Eq. (2) and involves two principal points:

(i) No change in oxidation state of the guest cations on the transfer from the electrolyte into the host matrix across the electrolyte/solid interface.

(ii) Quantitative transfer of the electrons involved into the lowest lying vacant energy level of the host matrix.

This obviously includes the assumption that a rigid band model presents an adequate description of the variation of the electronic structure with the change in charge transfer. The maximum uptake of guest ions into the host lattice will thus be governed primarily by the following factors: (i) electronic aspects, i.e., the band structure of the solid and (ii) steric limitations, lattice strain effects and mutual Coulomb repulsion of guest cations.

The metal ions that have been found to intercalate in appropriate host lattices at room temperature can be divided into two groups. The *monovalent* species belong to group IA (lithium to cesium), group IB (Cu, Ag) and group IIIA (Tl). Among these Li and Na have attained special attention with respect to reversible battery electrode systems, since both cations exhibit high ionic mobilities and high free energies of reaction with a number of oxide and chalcogenide host lattices.[43] *Bivalent* transition metal ions have been shown to intercalate in molybdenum chalcogenides Mo_6X_8 (X = S, Se, Te); for reasons discussed below they represent a particularly interesting case. We shall therefore start the discussion with these systems and then continue to consider intercalation compounds with monovalent ions.

The rhombohedral binary molybdenum chalcogenides Mo_6X_8 (Chevrel phases) are metallic conductors; they are characterized by a framework lattice with intersecting channels of empty lattice sites. Ternary phases $A_xMo_6X_8$ (A = transition or main group metal) can be prepared at higher temperatures.[12,13] Recently it has been shown that the binary compounds represent host lattices suitable for reversible intercalation reactions by electron/ion transfer according to the scheme given in Eq. (3). They are able to intercalate monovalent and bivalent guest ions to an upper critical size determined by the effective channel diameter[6,7,14]:

$$x\,A^+ + x\,e^- + [Mo_6X_8] \rightleftarrows A_x\,[Mo_6X_8]. \tag{3}$$

One of the unusual phenomena exhibited by these phases is the fact that the bivalent guest cations have a rather high mobility at ambient temperature.[14] The activation energies for transport of bivalent cations in solids must be significantly higher, however, than those for monovalent ions. Although in the case of electronic/ionic conductors one should expect somewhat lower activation energies because of the mobile negative screening charges, no room temperature electrolyte for bivalent cations has been reported so far except for Mo_6X_8 as the host lattice. We shall see below that there exists, however, an explanation for this unusual behavior that is related to the electron distribution.

To explain the stoichiometry of the phases $A_xMo_6X_8$ (prepared by thermal methods) a model has been proposed recently[12] based on an ionic/covalent bonding scheme $A^{n+}_{x/n}$ $[Mo_6S_8]^{x-}$ which has been used also for the description of related systems.[15] The maximum transfer number x of electrons to the host matrix predicted by this scheme corresponds to $4e^-/Mo_6X_8$; band structure calculations support this model.[16] The experimental data including structural and physical properties obtained for thermal phases have been discussed in terms of this concept.

Recent studies on the intercalation of metal ions in Mo_6X_8 phases yielded results which did not seem to fit into this scheme.[17] The first observation of this kind was made in an investigation of the electrochemical intercalation of Ni^{2+} ions from aqueous electrolyte in Mo_6S_8. In Figure 2 the potential charge transfer diagram is given for the coulometric titration of Mo_6S_8 electrodes in Ni^+/H_2O at pH eq 3.5. The total charge transfer amounts to $6e^-/Mo_6S_8$, i.e., two electrons more than allowed by the band structure. Extended studies revealed that range I (Figure 2) is a two-phase region related to the formation of $Ni_1Mo_6S_8$ [Eq. (4)]. Range II corresponds to a nonstoichiometric region in which Ni^{2+} and protons are intercalated simultaneously to yield $Ni_2H_2[Mo_6S_8]$ at the upper phase limit [Eq. (5)].

$$Mo_6S_8 + Ni^{2+} + 2\,e^- \rightleftarrows Ni_1\,[Mo_6S_8]. \qquad (4)$$

$$Ni^{2+} + 2\,H^+ + 4\,e^- + Ni_1\,[Mo_6S_8] \rightleftarrows (Ni_2H_2)[Mo_6S_8]. \qquad (5)$$

Since according to the model cited above the host lattice band structure accepts a maximum of $4e^-$, it is reasonable to conclude that at least two of the six electrons transferred have to be stored in guest-guest covalent bonds. In the ionic description $[Ni_2H_2]^{n+}$ $[Mo_6S_8]^{n-}$ the magnitude of

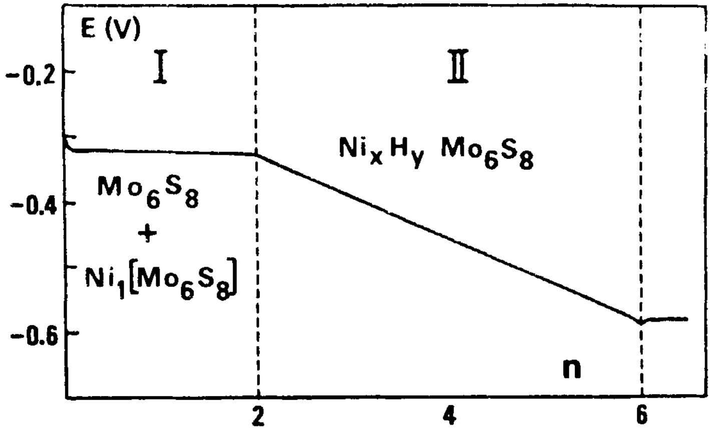
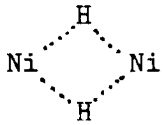


FIGURE 2 Cathodic reduction of Mo_6S_8 in Ni^{2+}/H_2O. E = potential of Mo_6S_8 electrode vs Ag/AgCl; n = e^-/Mo_6S_8.

n can only be <4. It was therefore assumed that hydrogen bridged Ni_2H_2 clusters are present inside the solid. Clusters of this type have been reported for a series of molecular hydride complexes of nickel.[18] A model with three electron/two center Ni/H bonding would thus lead to an effective charge of the guest cluster of +2 and a formal oxidation state for nickel of +1.



Evidence for the storage of electrons in covalent metal–metal bonding of guest ions has been found also in the case of the zinc and cadmium compounds $Zn_2Mo_6S_8$ and $Cd_2Mo_6S_8$.[17] If the guest metal ions were considered bivalent the ionic formula would correspond to $(Zn^{2+})_2[Mo_6S_8]^{4-}$ and $(Cd^{2+})_2[Mo_6S_8]^{4-}$ in agreement with the maximum charge transfer allowed. Both phases were shown to be superconductors at low temperatures. From theoretical and experimental evidence it is known, however, that the complete filling of the upper band with four electrons is correlated with the transition to a semiconductor state. It was concluded therefore that two of the electrons transferred are stored in guest ion cluster metal–metal bonds A–A and that the correct description is given by the formula

$$(Zn_2)^{2+}\ [Mo_6S_8]^{2-} \qquad (Cd_2)^{2+}\ [Mo_6S_8]^{2-},$$

with a formal oxidation state of +1 for the guest ions.

If we assume a similar formation of $(M_2)^{2+}$ metal cluster complexes for the other intercalation compounds of Mo_6X_8 with small transition metal ions we have a reasonable model that is able to explain the high ionic conductivity of these phases at ambient temperature. The mobile species are monovalent M^+ ions resulting from dissociation equilibria:

$$(M_2)^{2+} \rightleftarrows 2\,M^+.$$

This concept is in agreement with the low free energy of formation of these compounds[7] and with the short metal–metal distances (~250 pm) as deduced from single crystal x-ray diffraction studies of thermal phases at low temperatures.[12,13]

It should be noted that in the case of the thermal phase $Ni_1Mo_6S_8$ a valency of +1 has been attributed to Ni, while no explanation was given for this assignment.[19] In a recent analysis of bonding in the ternary Chevrel type chalcogenides in terms of the "Pauling bond order sum per electron" covalent Mo–A bonding has been proposed between the guest species Fe, Co, Ni—which were considered as bivalent ions—and the molybdenum atoms of the host matrix.[20] However, this scheme would not account for the high mobility of these ions unless one assumed a low lying excited configuration state $\mathrm{Fe}^{2+} + e^- \rightleftarrows \mathrm{Fe}^+$ for the relaxation process.

Intercalated *alkali metals* usually exhibit rather high mobilities in various host lattices. Although these guest ions have very low ionization energies, stoichiometry dependent changes in the charge transfer have been described for several systems. Fractional charge transfer in alkali metal/graphite intercalation compounds has been discussed early.[21–23] Graphite has a low electron affinity and the $\Delta_R G$ values for the alkali metal intercalation compounds are small. NMR studies[9] show that compounds with small alkali concentration (higher stage phases with alkali atoms filling in a regular sequence only a part of the van der Waals gaps between the graphite layers) can be described by quantitative charge transfer. For the first stage phases with maximum alkali content $\mathrm{LiC_6}$ and $\mathrm{AC_8}$ (A = K, Rb, Cs) strong Knight shift is observed, however. An ionic character of ~60% was estimated for the strongly electropositive metals K, Rb and Cs. In analogy with the situation discussed above for the molybdenum chalcogenides we propose a model based on the idea that the excess *s* electrons not transferred to the graphite matrix band are stored in covalent metal–metal bonds of guest cluster units, i.e., electron deficient multicenter bonding. At ambient temperature K, Rb and Cs are mobile and clusters A_n^{x+} ($x < n$) of different size and geometry are thought to be present in temperature dependent dissociation equilibria.[7]

The situation seems to be quite different for the lithium compound $\mathrm{LiC_6}$. The Li-NMR data which indicate quadrupole splitting and strong Knight shift have been interpreted in terms of partial covalent bonding of the guest atoms to the graphite matrix, i.e., partial charge transfer due to electron storage now in host/guest covalent bonding. The fact that no pure first stage sodium/graphite phase exists can be explained by a borderline situation: Sodium is neither able to form covalent carbon/metal bonds like the small lithium atoms nor able to engage in metal/metal bonding like the more electropositive alkali metals with larger radius.

Similar observations of stoichiometry dependent ionicity of alkali metal guest ions have been reported for chalcogenide host lattices. The layered transition metal chalcogenides MX_2 are able to take up alkali metals into the van der Waals gap:

$$x\,A^+ + x\,e^- + MX_2 \rightleftarrows A_x^+[MX_2]^{x-}. \tag{6}$$

The appearance of higher stage compounds and of transitions between octahedral and trigonal prismatic coordination for A are related to the stoichiometry x, the size of A and the nature of the host lattice.[2,24] Li- and Na-NMR studies give evidence that the ionicity of A changes with stoichiometry: At low metal concentrations quantitative ionization of A is observed, while at higher concentration up to $x = 1$ (all octahedral sites filled) residual s-electron density remains at the guest metal atoms; the estimated fractional ionization amounts to ~80%–90%. This change in ionicity is correlated in some cases with structural and electronic phase transitions. The group VIB metal chalcogenides have particularly low stability which is due to the fact that the d_z2 band of the host lattice (Figure 3) is filled up and electrons donated to the solid have to be accommodated in higher levels. Several lithium phases have been reported recently which show that one additional lithium can be intercalated to give Li_2MS_2 (M = Ti, V).[25]

$$Li_1MX_2 + Li^+ + e^- \rightleftarrows Li_2[MX_2]. \tag{7}$$

The $\Delta_R G$ values for the formation of these compounds are rather low and lithium must at least partially occupy tetrahedral sites. It is likely that the additional electrons are stored in metal–metal bonds of guest clusters Li_n^{x+} $(x < n)$.

Stoichiometry dependent changes in bonding were also observed for $Li_x[Mo_6Se_8]$ by Li-NMR. $Li_1[Mo_6S_8]$ shows no Knight shift (relative to Li^+/H_2O) but strong quadrupolar splitting; conversely, for $Li_4[Mo_6Se_8]$ strong Knight shift is observed but no quadrupolar splitting. The results can be interpreted in terms of Li_4^{3+} guest clusters or chains Li_n^{x+} $(x < n)$ with electron deficient multicenter metal–metal bonding.[26] Dissociation equilibria account for the high mobility of lithium at room temperature. Theoretical and experimental evidence for the existence of alkali metal clusters in solids, e.g., Li_3^+ and Na_4^{3+}, has been discussed in several studies.[27]

Intercalation compounds with copper are known for various host lattices (MX_2, Mo_6X_8, V_2O_5). The free enthalpies of formation are

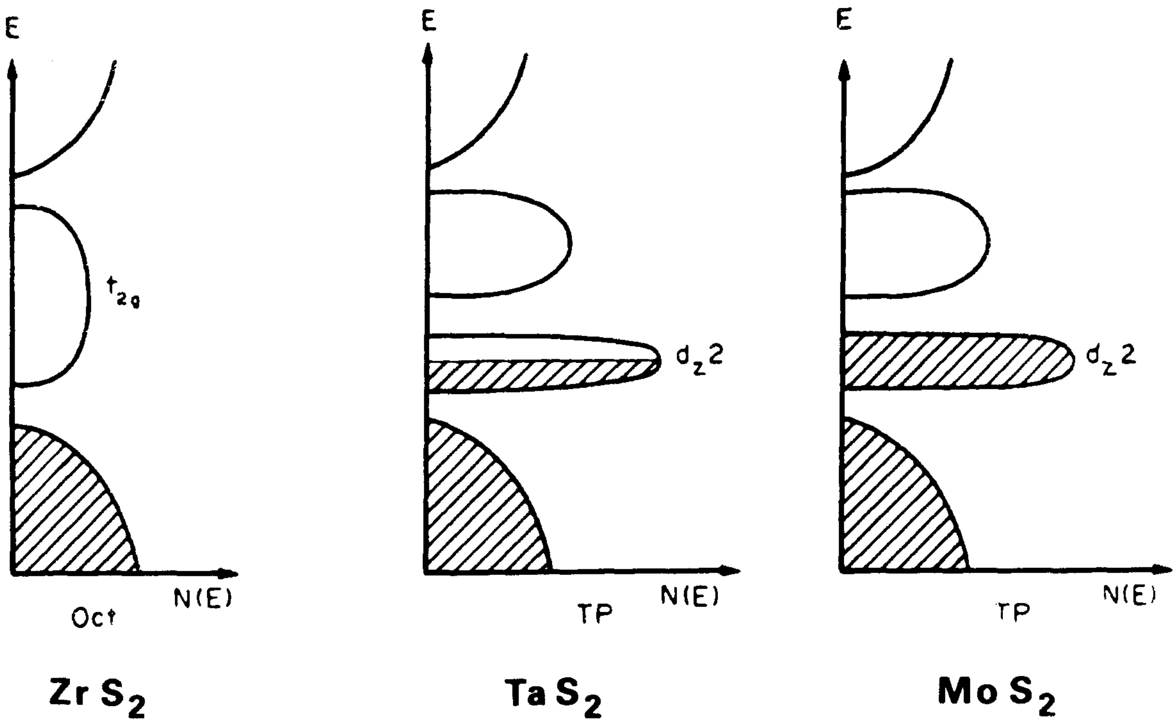


FIGURE 3 Band structure scheme of group IVB, VB and VIB metal dichalcogenides with layered structures.

generally low. Copper is present in these phases as monovalent species and prefers (distorted) tetrahedral sites. The existence of low lying *d/s* hybrid excited states[28] can explain the relatively high mobility of these guest ions at room temperature. Cu(I) has a general tendency to engage in covalent bonds which could be formed in intercalation compounds either with the host lattice anions or with neighboring Cu atoms at high guest ion concentration. Copper cluster compounds Cu_n ($n = 2$–8) are well known from molecular complexes and MO calculations support the existence of attractive Cu–Cu interactions in these clusters.[29] Similar considerations apply to Ag^+ intercalation compounds.

Covalent bonding to the host lattice must play a role in hydrogen bronzes.[6,7] The intercalation of hydrogen by electron/proton transfer is still a largely unexplored interesting field and there is no satisfying explanation at the moment for the strong differences in activation energies observed (mechanism of proton transfer) for various hydrogen bronzes and the appearance of low dimensional mobility of hydrogen, e.g., in H_xMoO_3 and H_xWO_3.[30]

Recently an example has been found for an unusual border case, i.e., a topotactic reaction with *no charge transfer* to the host matrix.[9,26] The thallium vanadium sulfide $Tl[V_5S_8]$ is a metallic conductor with Tl atoms in isolated parallel lattice channels which are mobile at 300 K. $Tl[V_5S_8]$ can be oxidized electrochemically in a reversible reaction to $Tl_{1/3}[V_5S_8]$. ^{205}Tl- and ^{51}V-NMR studies have demonstrated that the charge on the V_5S_8 matrix remains constant on oxidation whereas the average oxidation state of the guest cations is changing from +1 to +3 according to Eq. (8):

$$Tl^{1+}[V_5S_8]^{1-} \rightleftharpoons (Tl^{3+})_{1/3}[V_5S_8]^{1-} + 2/3\ Tl^{3+} + 2\ e^-. \qquad (8)$$

This redox reaction thus represents the extreme case of a stoichiometry dependent change in the oxidation state of the guest ions while the host lattice excess charge remains constant.

If we now summarize the elements of the foregoing discussion, we may describe charge transfer processes in topotactic redox reactions with metal guest species in the following scheme:

(1) *quantitative charge transfer* to the host lattice matrix ($\Delta_R G$ high) favored by

- high electron affinity E_A of the host lattice
- low ionization energy E_I of the guest species
- low guest metal content

(2) *partial charge transfer* ($\Delta_R G$ low) favored by

- low E_A of the host lattice
- high E_I of guest species
- high guest metal content

Two different bonding situations can be distinguished:

(i) electrons stored in guest–guest bonding (either two electron bonds or electron deficient multicenter bonding):

- enforced if band is filled up (e.g., $Ni_2H_2[Mo_6S_8]$)
- favored by the nature of the guest species (e.g., Zn, Cd in Mo_6X_8)

(ii) electrons stored in host/guest covalent bonding (e.g., H in hydrogen bronzes, Li in LiC_6)

(3) *no charge transfer* to the host matrix; the redox reaction proceeds exclusively via stoichiometry dependent changes of the oxidation state of the guest cations (e.g., $Tl^+ \rightleftarrows Tl^{3+} + 2\,e^-$).

A series of systems exists where the mode of charge transfer is still largely unclear. One example is the intercalation of alkali metal ions in transition metal phosphorous chalcogenides such as $NiPS_3$ or $CrPS_4$.[2] For Li_xNIPS_3 the storage of electrons in antibonding phosphorus orbitals has been suggested. Relatively few band structure calculations have been reported for host lattices. There is evidence that in certain cases intercalation is related to significant changes in the electronic band structure, i.e., the rigid band model approximation becomes invalid.

MOLECULAR GUEST SPECIES

A large variety of inorganic, organic and metal organic molecular guest ions can be intercalated via electron/ion transfer reactions into *layered* lattices, since the latter are able to adapt readily to the size of the guests.[1,4–8]

One particular type of reaction has been under discussion for some time with respect to the nature of the interaction host lattice/guest species. This concerns the observation that a large number of neutral molecules with Lewis base character (e.g., NH_3, aliphatic and aromatic amines and amides, nitrogen heterocycles) can be intercalated thermally in neutral empty layered host lattices with electronic conductivity:

$$NH_3 + TaS_2 \rightarrow (NH_3)_1TaS_2; \tag{9}$$

$$1/2\ C_5H_5N + TaS_2 \rightarrow (C_5H_5N)_{1/2}TaS_2. \qquad (10)$$

In the case of the transition metal dichalcogenides the original bonding model was based on Mulliken-type charge transfer (low lying excited states) from the Lewis base guest molecule to the empty or half filled d_z2 band of the host lattice[31] under conservation of the structural integrity of the guest species. Subsequent studies were able, however, to show that a fraction of the guest molecules undergo redox reactions resulting in products with ionic structure and cointercalated neutral molecules interacting with the guest ions via ion/dipole forces.[6,10,11] The intercalation of, e.g., NH_3 and pyridine (py) has to be described by the following scheme:

$$\begin{array}{c}
2\ NH_3 \rightarrow N_2 + 6H^+ + 6e^- \\
H^+ + NH_3 \rightarrow NH_4^+ \\
xe^- + TaS_2 \rightarrow [TaS_2]^{x-} \\
\hline
\text{product formula:} \\
(NH_4^+)_x(NH_3)_y[TaS_2]^{x-}
\end{array}$$

$$\begin{array}{ll}
x\ \text{py} & \rightarrow (x/2)(\text{py} - \text{py}) + xH^+ + xe^- \\
H^+ + \text{py} & \rightarrow \text{py}\ H^+ \\
xe^- + TaS_2 & \rightarrow [TaS_2]^{x-} \\
\hline
\multicolumn{2}{c}{\text{product formula:}} \\
\multicolumn{2}{c}{(\text{py}H^+)_x(\text{py})_{0.5-2x}(\text{py} - \text{py})_{x/2}[TaS_2]^{x-}}
\end{array}$$

Dinitrogen and dipyridine (py − py) are formed as the reaction products of the molecular redox disproportionation. These reactions can be more complex for larger guest molecules and different ionic species may be found. Similar redox disproportionation has been reported also for the intercalation reactions of neutral Lewis bases with other host lattices, e.g., FeOCl and MoO_3.[7,32]

It is easy to conclude that a border case with direct ionization of the neutral guest species should exist if molecules with sufficiently low ionization energies are intercalated. This has been demonstrated for a series of metallocenes $(C_5H_5)_2M$ and $(C_6H_6)_2M$ (M = transition metal) which react according to Eq. (11) under conservation of the molecular integrity of the guest molecules[33]:

$$x(C_5H_5)_2Co + TiS_2 \rightarrow [(C_5H_5)_2Co^+]_x[TiS_2]^{+-}. \quad (11)$$

Graphite is exceptional as a host lattice, since it is able to intercalate at elevated temperatures a large number of metal halides MCl_n (e.g., $FeCl_3$, $AlCl_3$) in the presence of excess halogen which acts as an oxidant, producing holes in the upper graphite band level.[21,22] The products are thus characterized by a *macrocation* host matrix:

$$y\,MCl_n + (x/2)Cl_2 + nC \rightleftarrows (MCl_{n+x})^-(MCl_n)_{y-1}(C_n)^+. \quad (12)$$

Recent studies on these systems showed that in those cases where the presence of halogen is not required molecular redox disproportionation reactions lead to the formation of ionic species and charge transfer from the host band to the guest species. For the intercalation of AsF_5 the following reaction scheme has been established[34]:

$$3\,AsF_5 + 2\,e^- \rightarrow 2\,AsF_6^- + AsF_3; \quad (13)$$

$$nC \rightarrow (C_n)^{m+} + m\,e^-. \quad (14)$$

The border case would again be direct electron uptake of the guest species from the host band, provided the guest species had an adequately high electron affinity. This was found to be the case for OsF_6 intercalation which yields $[OsF_6]^- [C_8]^+$.[35] Similarly, the intercalation of Br_2 in graphite is thought to result in an ionic structure $(Br_m)^-(Br_2)_y[C_n]^+$ via charge transfer by the formation of anionic polyhalogen chains $(Br_m)^-$.

In summarizing we may distinguish between the following cases: (1) General case—the intercalation reaction involves complex molecular redox disproportionation processes. (2) Border Case—the intercalation proceeds via direct ionization or electron uptake of the guest species which in this case retain their molecular integrity. Conditions favorable for this type of reaction are (i) electron acceptor hosts—low ionization energy E_I of guest species, high electron affinity E_A of host lattice; (ii) electron donor hosts—high E_A of guest species, low E_I of host lattice. The present experimental evidence thus suggests that the general hypothesis discussed in the Introduction is also valid for the intercalation of neutral molecular guest species into host lattices with electronic conductivity.

Layered host lattices (transition metal dichalcogenides, MoO_3, α-$RuCl_3$) are able to intercalate solvated guest ions into the interlayer space [eq. (15); solv = polar neutral molecules, H_2O, NH_3, amines, acid amides, etc.].[36,37]

$$x\,A^+ + x\,e^- + y\,\text{solv} + [Z] \rightleftarrows (A^+)_x(\text{solv})_2[Z]^{x-}. \tag{15}$$

Guest cations can be metal ions or molecular ions (protonated Lewis bases, quaternary organic cations, metal complex cations). Higher valence metal ions (A^{2+}, A^{3+}) are also highly mobile at 300 K in the solvated state. The cations are strongly screened by the solvent molecules (ion/dipole interaction) and the experimental evidence available shows that in all cases quantitative charge transfer takes place. This pertains also to host lattices with low electron affinity such as MoS_2 (d_z2 band occupied, Figure 3) and graphite, although these phases have low stability.

A special case is the spontaneous reaction of transition metal dichalcogenides MX_2 with aqueous basic solutions, e.g., alkali hydroxides, quaternary ammonium hydroxides and Lewis bases with high K_B values. The intercalation proceeds here via partial irreversible solvolysis of the guest layers under formation of HS^- and S^{2-} which act as the electron donors and are oxidized to elemental sulfur or polysulfides, respectively[37]:

$$2x\,OH^- + MS_2 \rightarrow [MX_{2-x}O_x] + x\,S^{2-} + x\,H_2O; \tag{16}$$

$$x\,S^{2-} \rightarrow (x/8)\,S_8 + 2x\,e^-; \tag{17}$$

$$xe^- + [MS_{2-x}O_x] \rightarrow [MS_{2-x}O_x]^{x-}. \tag{18}$$

The products are solvated ionic phases $(A^+)_x$ $[MS_{2-x}O_x]^{x-}$ which may cointercalate neutral AOH ion pairs at high AOH concentration in the electrolyte.[38]

The general concept for electron/ion transfer reactions involves electronic conductivity of the host lattice. Two cases have been reported lately for solvated layered phases which are correlated with topotactic redox reactions in wide gap conductors. α-$RuCl_3$ can be reduced electrochemically up to an electron transfer of 0.5 $e^-/RuCl_3$, e.g., in Na^+/H_2O electrolyte[39]:

$$0.5\ \mathrm{Na^+} + y\ \mathrm{H_2O} + \mathrm{RuCl_3} \rightleftarrows (\mathrm{Na^+})_{0.5}(\mathrm{H_2O})_y[\mathrm{RuCl_3}]^{0.5-}. \quad (19)$$

Further reduction up to $[RuCl_3]^{1-}$ can only be accomplished chemically by treatment with sodium dithionite $Na_2S_2O_4$ and is related to an electronic transition from a semiconductor to an insulator state (yellow transparent) of the solid. This process can be explained on grounds of the Donnan equilibrium. A low equilibrium concentration of reducing $HS_2O_4^-$ anions is present inside the interlayer space so that the electron transfer to the bulk of the solid is not limited by the electronic transport properties of the solid (as is the case for electrochemical reduction). The same mechanism is likely to be responsible for the topotactic redox reactions observed for the layered vanadylphosphate $VOPO_4 \cdot 2H_2O$ (insulator).[40]

REACTION MECHANISM: LAYERED MATERIALS

The formation of intercalation compounds, regardless of the type or structural dimensionality of the host lattice, is usually connected with the appearance of intermediates (line phases or nonstoichiometric compounds). As a rule, there is a lower critical stoichiometry limit which can be understood basically in terms of lattice energy. The stoichiometries and ordering states of intermediates and final products must be related primarily to electronic aspects (band structure), electrostatic effects (attractive and repulsive Coulomb interactions) and strain energy (deformation of the host lattice upon intercalation). These points are not well understood at present. A further complication is the strong influence of kinetics on solid state reactions at low temperatures, especially if $\Delta_R G$ changes are small.

Specific ordering phenomena and phase transitions are found for layered host materials: stacking changes, i.e., changes in the relative position of the layers perpendicular to the basal planes, and "staging." The latter describes the fact that at low stoichiometries various phases may appear in which alternate van der Waals gaps are occupied or empty, respectively, in a regular sequence (Figure 4). This effect was detected originally for graphite compounds[21,22] but most other layered hosts exhibit similar behavior. A thermodynamic model for the description of this phenomenon has been given recently.[41] The puzzling observation of the transitions even/uneven stage was explained earlier by a domain model (Figure 4).[22]

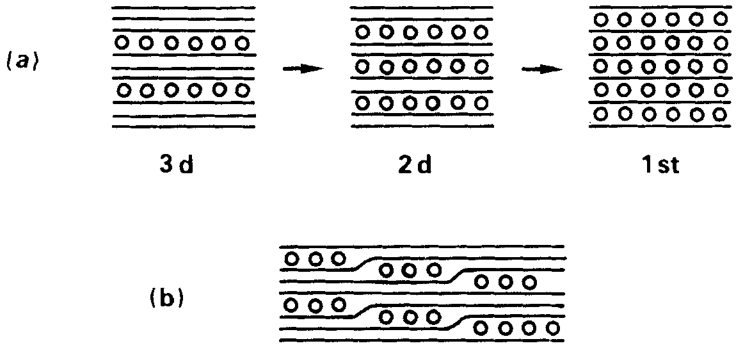


FIGURE 4 Scheme of staging in layered intercalation compounds. (a) sequence third to first stage, (b) domain model of third stage.

Hysteresis phenomena are characteristic for the formation of hydrated chalcogenides.[37,42] Upon intercalation of TiS_2 with $K^+(H_2O)_x$ by cathodic reduction close to the equilibrium potential the sequence

$$TiS_2 \rightarrow \text{3rd stage} \rightarrow \text{2nd stage} \rightarrow \text{1st stage}$$

is found. The formation of a third stage phase, which is a partially disordered domain stage, obviously proceeds with a lower activation than the expected 4th stage phase that requires a higher elastic deformation energy of the layers. On reversing the formation process by anodic oxidation the reaction proceeds via a partially disorderd 4th stage phase:

$$\text{1st stage} \rightarrow \text{2nd stage} \rightarrow \text{4th stage} \rightarrow TiS_2.$$

This *hysteresis* can be explained in terms of a model that involves differences in the activation energies (Figure 5). The reaction rate strongly influences this process: At high rates (overpotential) the third stage disappears and a sequence TiS_2 → 2nd stage → 1st stage is found on reduction.

DYNAMICS OF GUEST SPECIES: ANISOTROPY PHENOMENA

A significant and interesting aspect of practical importance is the correlation of the temperature-dependent mobility of guest species in electronic/ionic conductors with structure and bonding. Fast ion transport

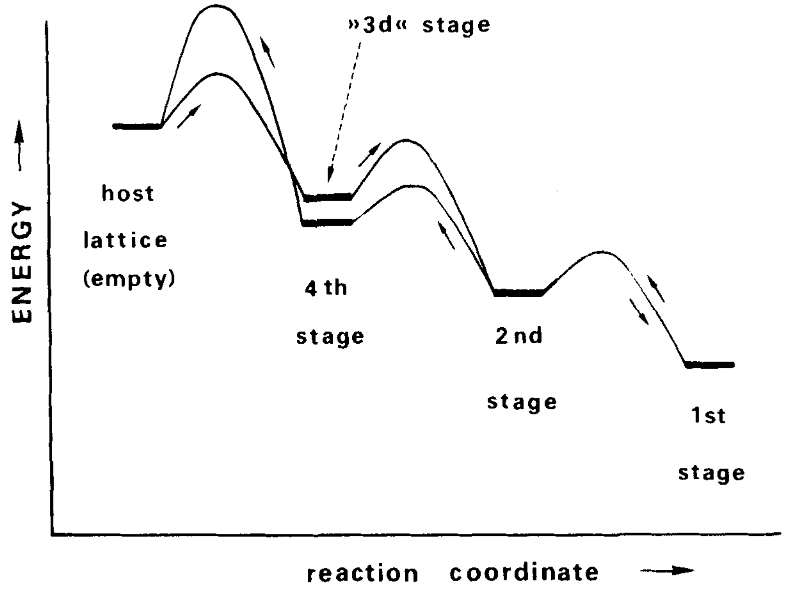


FIGURE 5 Energetic scheme of staging hysteresis.

in the host lattice is a prerequisite for the application of these systems, e.g., as reversible battery electrodes.[4,43] With respect to the large number of host lattices and guest species, few and often conflicting data have been published on ionic conductivity, chemical diffusion coefficients and activation energies for ionic transport. The development of theoretical models has been restricted primarily to solid insulator electrolytes,[44] which are different from electronic/ionic conductors due to charge screening (mobile host matrix charges).

A particular phenomenon is the observation of strong anisotropy effects in compounds with low-dimensional host lattices. An example for atomic guests is the quasi one-dimensional mobility of hydrogen in hexagonal H_xWO_3 and in H_xMoO_3 which is rather surprising, since H^+ ions have a very small size and could be envisaged to exhibit isotropic mobility in a host lattice with electronic conductivity.[30]

Extreme anisotropic mobility for *molecular* species was found in compounds of transition metal chalcogenides. NMR data show the signal for isolated two-spin systems in solvated monolayer phases $A^+_{1/3}$ $(solv)_{2/3}[MX_2]^{x-}$ with H_2O and H_2S as the solvate species due to ordered

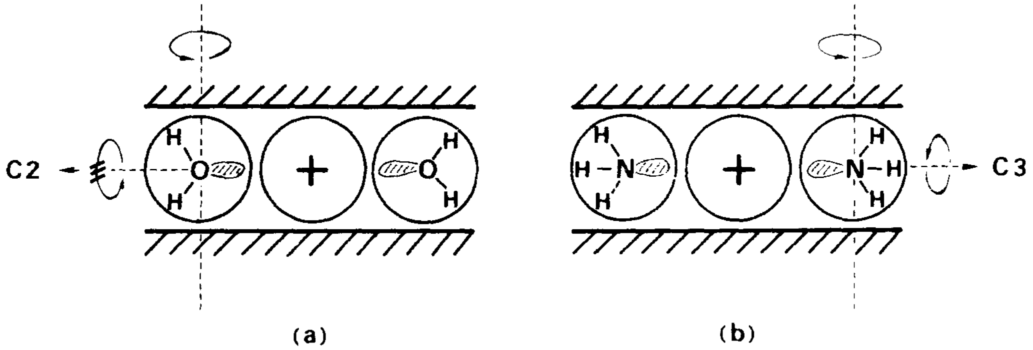


FIGURE 6 Anisotropic mobility of solvate molecules in layered chalcogenides $A_x^+(\mathrm{solv})_y\,[MX_2]^{x-}$. (a) solv = H_2O, H_2S; (b) solv = NH_3.

activated mobility at ambient temperature.[45] Two-dimensional translation is allowed, reorientation of the C2 axis of the solvate molecules is restricted to the midplane between adjoining MX_2 layers, and rotation around the C2 axis is inhibited (Figure 6). The translation to the rigid lattice state is dependent upon the solvation energy at A^+. Similar anisotropic mobility was observed for NH_3 in $(NH_3)MX_2$[46] and in $(A^+)_x(NH_3)_y[MX_2]^{x-}$.[26] The lower potential wells allow rotation of the NH_3 group around the C3 axis at 300 K (Figure 6). The behavior of isolated three-spin systems (NMR data) is also found for intercalation compounds of methylamines.[47] More complex guest dynamics were reported for larger guest species.[48]

CONCLUSIONS

Although the basic concept for intercalation reactions via electron/ion transfer appears to be most simple, the details can be rather complex for various reasons. Additional complications arise from the strong influence of kinetics on these solid state reactions.

It is obvious that further progress towards a quantitative understanding will require a broader base of structural studies (including ordering states and inherent lattice defects), theoretical work (band structure schemes, lattice strain energy) and new efforts to uncover the correlations between structure and mobility of guest species in electronic/ionic conductors. This will lead in turn to a better understanding of the interesting changes in physical properties (superconducting transitions, charge density waves, anisotropy phenomena) observed on intercalation and to a more efficient base for the selection and improvement of systems that are of interest with respect to application. We conclude that intercalation chemistry has become an important domain of solid state chemistry that provides many attractive features for future research activities.

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